

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Article 36 and Rule 70)

REC'D 24 FEB 2005

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Applicant's or agent's file reference 2001B124A	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US 03/18713	International filing date (<i>day/month/year</i>) 12.06.2003	Priority date (<i>day/month/year</i>) 12.12.2002
International Patent Classification (IPC) or both national classification and IPC C08F291/00		
Applicant EXXONMOBIL CHEMICAL PATENTS, INC. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets, including this cover sheet.
- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).
- These annexes consist of a total of 3 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the opinion
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 08.06.2004	Date of completion of this report 23.02.2005
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Giesemann, G Telephone No. +49 89 2399-8517 

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/US 03/18713**

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1, 3, 5-11, 13-31 as originally filed
2, 4, 12 received on 27.01.2005 with letter of 27.01.2005

Claims, Numbers

1-36 as originally filed

Drawings, Sheets

1/8-8/8 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

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5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	12-36
	No: Claims	1-11
Inventive step (IS)	Yes: Claims	12-36
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-36
	No: Claims	

2. Citations and explanations

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US 03/18713

- D1: EP-A-1 050 548 (CHEMPLAST MARKETING SERVICES E) 8 November 2000 (2000-11-08)
D2: EP-A-0 507 075 (BASF AG) 7 October 1992 (1992-10-07)
D3: EP-A-0 113 259 (CEAT STE FSE) 11 July 1984 (1984-07-11)
D4: US-A-5 169 900 (GUDELIS PAUL V) 8 December 1992 (1992-12-08)
D5: US-A-5 741 858 (CREE STEPHEN H ET AL) 21 April 1998 (1998-04-21)

1. D2 is considered the closest prior art document.
According to the Applicants, D2 does not teach vulcanization or final cross linking with water of the silane grafted resilient polymer as a separate step.
In support of this they refer to claims 12 and 20 to 23 as originally filed.
These claims are not suggested from the contents of D2 (Art. 33(3) PCT).
2. It is clear from the above that the presence of water is an essential feature which must be incorporated into the main claim 1 in order to make it clear what is actually claimed.
The objections against claims 1 to 11 as given in the official opinion must be maintained as long as the novelty feature "water" is not present in these claims - unless there is a further novelty feature in these claims 1 to 11 which is hitherto unknown (Art. 33(2) PCT).
3. D1 and D2 are acknowledged at new page 2. The other documents cited are only background art.

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polypropylene matrix. In a first step, the ethylene-octene polymers are coated and peroxide generation upon melting causes grafting (See *Polymer Engineering and Science* at page 1092). The polypropylene appropriately coated is added and blended in a second step. In a third step, water is injected to effect cross-linking.

5 DE4402943 discloses a similar process.

[0007] PCT publication WO 98/23687 discloses thermoplastic polymer blend compositions that include a thermoplastic matrix resin phase that is substantially free of cross-linking and a dispersed silane-grafted elastomer phase.

10 [0008] It is among the objects of the invention to provide a simplified and/or flexible process by integrating blending and grafting and/or blending and curing. EP-A-1 050 548 and EP-A-0 507 075 represent prior art grafted thermoplastic compositions.

3. SUMMARY OF THE INVENTION

15 [0009] In one embodiment, the present invention provides a process for making a thermoplastic vulcanizate ("TPV") in a reactor. The process includes forming a mixture in which a silane grafted resilient polymer component is dispersed in a thermoplastic matrix component and adding a solid water-generating agent to crosslink the silane grafted elastomer component. The mixture is formed by
20 mixing in the reactor: a) from 40 to 75 parts by weight of the matrix component, per 100 parts by weight of the matrix component and resilient polymer component combined, b) from 25 to 60 parts by weight of the resilient polymer component, per 100 parts by weight of the matrix component and resilient polymer component combined, and c) a silane grafting agent.

25 [0010] In another embodiment, the process includes a) blending a thermoplastic polymer component for forming a continuous matrix phase, a resilient polymer component, and a silane grafting agent for forming a phase dispersed in the matrix, and additives so as to promote silane grafting; and b) adding a solid water generating agent, which releases water, while the blend formed in step a) is
30 submitted to shear so as to crosslink the silane grafted polymer.

[0011] In a particular aspect of any of the embodiments described herein, the process has one or more of the following characteristics, in any combination:

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- q) the reactor is a continuous-type compounding apparatus;
- r) the reactor is connected to a die suitable for extruding the product in the reactor into a shaped, fabricated product without an intervening pelletization step;
- 5 s) the matrix component has a crystallinity as determined by DSC of at least 40%;
- t) the resilient polymer component has a crystallinity as determined by DSC of no more than 40%;
- u) the crystallinity of the matrix component and the resilient polymer component differ by at least 10%, or at least 20%; and
- 10 v) the matrix component and the resilient polymer component are blended and simultaneously combined with the silane grafting agent.

4. BRIEF DESCRIPTION OF THE DRAWINGS

- 15 [0012] Figure 1 is a graph of the thermogravimetric analysis of weight loss versus temperature for magnesium sulfate heptahydrate (Epsom salt).
- [0013] Figure 2 is a graph of the thermogravimetric analysis of weight loss versus temperature for sodium sulfate decahydrate (Glauber's salt).
- [0014] Figure 3 is a graph of the thermogravimetric analysis of weight loss
20 versus temperature for talc.
- [0015] Figure 4 is a graph of the thermogravimetric analysis of weight loss versus temperature for hydrated clay (hydrous aluminum silicate).
- [0016] Figure 5 is the thermogravimetric analysis of weight loss versus temperature for a zinc oxide/stearic acid combination.
- 25 [0017] Figure 6 is the thermogravimetric analysis of weight loss versus temperature for a zinc oxide/isononanoic acid combination.
- [0018] Figure 7 is the thermogravimetric analysis of weight loss versus temperature for a zinc oxide/isooctanoic acid combination.
- [0019] Figure 8 is a low voltage SEM micrograph of calendared sheeting.

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- [0042] When the silane grafting reaction is complete, a water-generating agent releases water upon heating, and preferably at the melting temperature range of the polymers, inside the compounding equipment, which enables the crosslinking to occur. The water-generating agent can be added to the reactor upon completion
- 5 of the silane grafting reaction. Examples of water-generating agents include Epsom salt, Glauber's salt, clay, water, talc, metal oxide/carboxylic acid combinations, and combinations thereof. Examples of metal oxide/carboxylic acid combinations are zinc oxide/stearic acid, zinc oxide/isononanoic acid, and zinc oxide isooctanoic acid.
- 10 [0043] Figures 1 and 2 illustrate the thermogravimetric analysis of weight loss versus temperature for magnesium sulfate heptahydrate (Epsom salt), and sodium sulfate decahydrate (Glauber's salt), respectively. The figures show that Epsom salt releases half of its hydrated water at 150°C to 200°C and Glauber's salt releases half of its hydrated water at a much lower temperature. Figures 3-7
- 15 illustrate the thermogravimetric analysis of weight loss versus temperature for talc, hydrated clay (hydrous aluminum silicate), and several metal oxide/carboxylic acid combinations (zinc oxide/stearic acid, zinc oxide/isononanoic acid, and zinc oxide/isooctanoic acid).
- [0044] In the presence of water molecules, the OR groups of the grafted
- 20 vinylsilane molecules can be easily hydrolyzed into OH groups. The Si-OH groups can then undergo a condensation reaction in the presence of a hydrolysis catalyst, for example dibutyltin dilaurate, to form Si-O-Si linkages. When there are not enough vinylsilane molecules grafted onto the elastomer backbone, the Si-O-Si linkages provide two dimensional chain extensions from the elastomer
- 25 molecules. When there are enough vinylsilane molecules grafted onto the elastomer backbone, a three dimensional network can be formed, and the elastomers are crosslinked. The crosslinking process described above is shown below.